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HANDBOOK OF DEPOSITION TECHNOLOGIES FOR FILMS AND COATINGS

**Science, Technology
and Applications**

Second Edition

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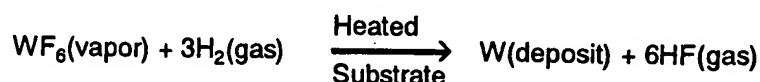
NOYES PUBLICATIONS

Westwood, New Jersey, U.S.A.

3. Steps in the Formation of a Deposit—There are three steps in the formation of a deposit:

- a. Synthesis or creation of the depositing species
- b. Transport from source to substrate
- c. Deposition onto the substrate and film growth

These steps can be completely separated from each other or be superimposed on each other depending upon the process under consideration. The important point to note is that if, in a given process, these steps can be individually varied and controlled, there is much greater flexibility for such a process as compared to one where they are not separately variable. This is analogous to the degrees of freedom in Gibbs phase rule. For example, consider the deposition of tungsten by CVD process. It takes place by the reaction:



The rate of deposition is controlled by the substrate temperature. At a high substrate temperature, the deposition rate is high and the structure consists of large columnar grains. This may not be a desirable structure. On the other hand, if the same deposit is produced by evaporation of tungsten, the deposition rate is essentially independent of the substrate temperature so that one can have a high deposition rate and a more desirable microstructure. On the other hand, a CVD process may be chosen over evaporation because of considerations of *throwing power*, i.e., the ability to coat irregularly shaped objects, since high vacuum evaporation is basically a line-of-sight technique.

5.0 PHYSICAL VAPOR DEPOSITION (PVD) PROCESS TERMINOLOGY

The basic PVD processes are those currently known as evaporation, sputtering and ion plating. In recent years, a significant number of specialized PVD processes based on the above have been developed and extensively used, e.g., reactive ion plating, activated reactive evaporation, reactive sputtering, etc. There is now considerable confusion since a particular process can be legitimately covered by more than one name. As



an example, if the *activated reactive evaporation* (ARE) process is used with a negative bias on the substrate, it is very often called *reactive ion plating*. Simple evaporation using an RF heated crucible has been called *gasless ion plating*. An even worse example of the confusion that can arise is found in the chapter on ion plating in this volume (Ch. 6) where the material is converted from the condensed phase to the vapor phase using thermal energy (i.e., evaporation) or momentum transfer (i.e., sputtering) or supplied as a vapor (very similar to CVD processes). Carrying this to the logical conclusion, one might say that all PVD processes are ion plating! On the other hand, the most important aspect of the ion plating process is the modification of the microstructure and composition of the deposit caused by the ion bombardment of the deposit resulting from the bias on the substrate, i.e., what is happening on the substrate.

To resolve this dilemma, it is proposed that we consider all of these basic processes and their variants as PVD processes and describe them in terms of the three steps in the formation of a deposit as described above. This will hopefully remove the confusion in terminology.

Step 1: Creation of Vapor Phase Species. There are three ways to put a material into the vapor phase—evaporation, sputtering or chemical vapors and gases.

Step 2: Transport from Source to Substrate. The transport of the vapor species from the source to the substrate can occur under line-of-sight or molecular flow-conditions (i.e., without collisions between atoms and molecules); alternately, if the partial pressure of the metal vapor and/or gas species in the vapor state is high enough or some of these species are ionized (by creating a plasma), there are many collisions in the vapor phase during transport to the substrate.

Step 3: Film Growth on the Substrate. This involves the deposition of the film by nucleation and growth processes. The microstructure and composition of the film can be modified by bombardment of the growing film by ions from the vapor phase resulting in sputtering and recondensation of the film atoms and enhanced surface mobility of the atoms in the near-surface and surface of the film.

Every PVD process can be usefully described and understood in terms of these three steps. The reader is referred to Chapter 9 for a more comprehensive treatment.

6.0 CLASSIFICATION OF COATING PROCESSES

Numerous schemes can be devised to classify or categorize coating processes, none of which are very satisfactory since several processes will overlap different categories. For example, the Appendix contains a list and definitions of various deposition processes based upon those provided by Chapman and Anderson with some additions. These authors classify the processes under the general heading of Conduction and Diffusion Processes, Chemical Processes, Wetting Processes and Spraying Processes. Here, the Chemical Vapor Deposition process falls under the Chemical Processes, and the Physical Vapor Deposition Process (Evaporation, Ion Plating and Sputtering) falls under the spraying processes. The situation can easily get confused as, for example, when Reactive and Activated Reactive Evaporation, and Reactive Ion Plating are all classified as Chemical Vapor Deposition processes by Yee^[3] who considers them thusly because a chemical reaction is involved and it does not matter to him whether evaporated metal atoms or stable liquid or gaseous compounds are the reactants. Another classification of the methods of deposition of thin films is given by Campbell.^[4] He considers the overlap between physical and chemical methods, e.g., evaporation and ion plating, sputtering and plasma reactions, reactive sputtering and gaseous anodization.^[5] He classifies the Chemical Methods of Thin Film Preparation as follows:

Chemical Methods of Thin Film Preparation

Basic Class	Method
Formation from the Medium	Electroplating Ion Plating Chemical Reduction Vapor Phase Plasma Reaction
Formation from the Substrate	Gaseous Anodization Thermal Plasma Reduction

In addition, he considers the following as chemical methods of thick film preparation: Glazing, Electrophoretic, Flame Spraying and Painting.

In contrast to the chemists' approach given above, the physicists' approach to deposition processes is shown in the following classification of vacuum deposition techniques by Schiller, Heisig and Goedicke^[6] and by Weissmantel.^[7]

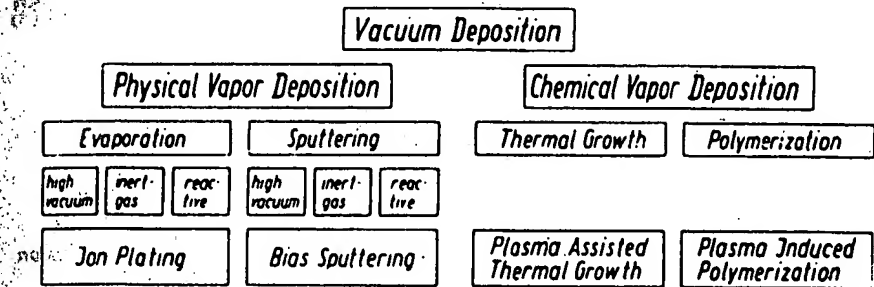


Figure 1.1. Survey of vacuum deposition techniques (Schiller^[6])

A different classification comes from a materials background where the concern is with structure and properties of the deposits as influenced by process parameters. Thus, Bunshah and Mattox^[8] give a classification based on deposition methods as influenced by the dimensions of the depositing species, e.g., whether it is atoms/molecules, liquid droplets or bulk quantities, as shown in Table 1.1.

In atomistic deposition processes, the atoms form a film by condensing on the substrate and migrating to sites, where nucleation and growth occurs. Further, adatoms do not achieve their lowest energy configurations and the resulting structure contains high concentrations of structural imperfections. Often the depositing atoms react with the substrate material to form a complex interfacial region.

Another aspect of coatings formed by atomistic deposition processes is as follows. The sources of atoms for these deposition processes can be by thermal vaporization (vacuum deposition) or sputtering (sputter deposition) in a vacuum, vaporized chemical species in a carrier gas (chemical vapor deposition), or ionic species in an electrolyte (electrodeposition). In low energy atomistic deposition processes, the depositing species impinge on the surface, migrate over the surface to a nucleation site where they condense and grow into a coating. The nucleation and growth modes of the condensing species determine the crystallography and microstructure of